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FINAL REPORT

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Report Prepared by:

George W. Watt, Project Director

August 31, 1953

Department of Chemistry
The University of Texas
Austin, Texas

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FINAL REPORT

Project NR 052 154

Contract N6onr-26610

Department of Chemistry,
The University of Texas

August 31, 1953
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Foreword

This report covers work carried out during the period September 1, 1948 to August 31, 1953. Throughout this period, Status Reports have been issued quarterly and Technical Reports have been issued as of September 1 in the years 1949, 1950, 1951, and 1952.

At its inception, it was the purpose of this program to prepare catalytically active metals of Periodic Group VIII by the reduction of appropriate salts by means of solutions of metals in liquid ammonia and to compare their physical properties with particular emphasis upon their activity as hydrogenation catalysts. Although the anticipated work on these metals is by no means complete, a considerable body of new information concerning eight of the nine metals has been obtained. An application for a patent covering this particular method for catalyst preparation has been filed with the U. S. Patent Office (Serial No. 309,147; September 11, 1952).

As this work progressed, study of the reduction reactions necessary for catalyst preparation brought to light certain interesting information relative to unusual oxidation states of the Group VIII transitional metals. Accordingly, during the latter part of the period covered by this report, the emphasis was shifted in part to include work on potentiometric titrations designed to yield information concerning oxidation states and reduction reaction mechanisms.

Because much of the work done under this contract has been published or is in the process, this report consists of (a) reprints of published papers, and (b) abstracts of papers that are presently "in press" and of papers that have either been submitted for publication or are currently being written. As reprints of papers in category (b) become available, they will be submitted as supplements to this report in order that the record may be complete. These items are listed in the Table of Contents under appropriate headings.

The experimental work covered in this report was done almost entirely by graduate students whose names appear as co-authors of papers published or planned for publication. The extent to which financial support received under this contract has contributed to improved opportunities for graduate study and accelerated research

training of students is, in the opinion of the writer, by no means a minor aspect of support of academic research by agencies of the federal government. Listed below are the names and present professional connections of those whose training has benefited by the existence of this research contract.

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Finally, the writer wishes to express his gratitude to the Office of Naval Research for the financial support received and for the freedom that has been allowed in determining the course of this program. Particular thanks are due Dr. L. W. Butz, Dr. Ralph Roberts, Mr. J. A. Bryson, and Mr. F. M. Lucas for their assistance and fine spirit of cooperation.

George W. Watt, Project Director

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[Contribution from the Department of Chemistry of the University of Texas]

The Action of Liquid Ammonia Solutions of Potassium and Potassium Amide upon Iron(II) Bromide[1]

By George W. Watt and W. A. Jenkins, Jr.[2]

Treatment of iron(II) bromide with potassium in liquid ammonia at −33.5° yields an ammonia-insoluble product consisting of elemental iron, iron(I) nitride, and one or more products of the interaction of iron(II) bromide and potassium amide. The iron produced in these reactions is pyrophoric, does not contain adsorbed hydrogen, has a surface area of 8 m.²/g., and is inactive as a catalyst for the hydrogenation of certain olefins at 30° and a hydrogen pressure of 2 atm.

The experiments described in this paper represent a continuation of studies on the reduction of salts of Group VIII elements to the corresponding metals by means of solutions of metals in liquid ammonia.[3] In these studies, emphasis is placed upon the properties of the reduction products, particularly with reference to their activity as hydrogenation catalysts.

Experimental

Materials.—With the exception noted below, all chemicals used in this work were reagent grade products used without further purification or were the same as those described previously.[3]

Iron(II) bromide was used in the form of the 6-ammonate which was prepared by a method that will be described elsewhere.[4]

Anal. Calcd. for $FeBr_2 \cdot 6NH_3$: Fe, 17.6; NH_3, 32.1. Found: Fe, 17.9; NH_3, 32.2.

Experimental Methods.—Unless otherwise specified, equipment and techniques employed were the same as those described earlier.[3] Reactions involving ammonia solutions of potassium were carried out in an apparatus of the type described by Watt and Moore[5]; those employing ammonia solutions of potassium amide were effected in equipment described by Watt and Keenan.[6] Electron photomicrographs were obtained using an RCA Type EMU-1 electron microscope; samples in Parlodion film were mounted on 200 mesh screen.[7]

The Reaction between Iron(II) Bromide and Potassium.—In a typical case, 2.932 g. of iron(II) bromide 6-ammonate suspended in 25–30 ml. of anhydrous liquid ammonia was treated with 1.209 g. of potassium ($K/FeBr_2 = 3.35$) added in one portion. All of the potassium reacted within 10 sec., hydrogen evolution was continuous throughout the total reaction time, and the bromide was converted to a black finely divided solid. The pale yellow supernatant solution was removed, the solid washed five times with 25-ml. portions of ammonia, resuspended in 25–30 ml. of ammonia, and treated with an additional 0.598 g. of potassium ($K/FeBr_2 = 1.66$). Again, hydrogen evolution was continuous, but there was no visual evidence of change in the solid phase. The ammonia-insoluble solid was washed with liquid ammonia until the washings were free of bromide ion and thereafter dried for 20 hr. at room temperature and a pressure of 0.1 mm. The resulting black solid was highly pyrophoric; qualitative tests for bromide ion were negative. Data relative to these reactions are given in Table I; variation in reaction ratios and mode of addition of potassium failed to alter appreciably the composition of the ammonia-insoluble products.

Table I

Reduction of Iron(II) Bromide with Potassium

$FeBr_2 \cdot 6NH_3$, g.	K, g.	$K/FeBr_2$	H_2, cc.	Insoluble product Fe, %	Insoluble product N, %
2.264	0.656[a]	2.36	83.7	76.6	6.2
2.932[b]	1.209	3.35	225.6		
	0.598	1.66	121.6	80.6	5.7
3.020	.846	2.28	106.4		
	.848	2.28	209.4	80.5	5.0
3.117[c]	.862	2.21	108.0		
	.947	2.47	211.9	82.3	7.1
2.243[d]	.875[a]	3.40	153.0	84.6	3.6

[a] One addition of potassium. [b] The insoluble product was analyzed for potassium. Found: 9.7%; total accounted for, 96.0%. [c] Potassium content of insoluble product, 6.5%; total accounted for, 95.9%. [d] Initial volume was 12–15 ml. rather than 25–30 ml.

The Reaction between Iron(II) Bromide and Potassium Amide.—In the course of efforts to identify products formed in the reduction of iron(II) bromide with potassium, the reaction between this salt and potassium amide was studied. A suspension of 2.702 g. of iron(II) bromide 6-ammonate in 50 ml. of ammonia was treated with 10 ml. of ammonia solution containing the potassium amide equivalent to 0.719 g. of potassium. The bromide was immediately and completely converted to a black insoluble solid which was washed and dried as described above. This product also was markedly pyrophoric.

Anal. Found: Fe, 61.0; N, 15.9; K, 8.7.

Preparation of Potassium Amide.—In order to obtain samples for X-ray diffraction patterns, potassium amide was prepared by the iron-catalyzed interaction of potassium and liquid ammonia.

Anal. Calcd. for KNH_2: K, 70.5. Found: K, 69.9.

X-Ray Diffraction Patterns.—As a means of identifying the products of the reduction of iron(II) bromide, X-ray

(1) This work was supported, in part, by the Office of Naval Research, Contract N6onr-26610.

(2) Radiation Laboratory, The University of California, Berkeley, California.

(3) G. W. Watt, W. F. Roper and S. G. Parker, This Journal, forthcoming publication.

(4) G. W. Watt and W. A. Jenkins, Jr., "Inorganic Syntheses," Vol. IV.

(5) G. W. Watt and T. E. Moore, This Journal, 70, 1197 (1948).

(6) G. W. Watt and C. W. Keenan, *ibid.*, 71, 3833 (1949).

(7) The assistance of Mr. L. L. Antes is gratefully acknowledged.

diffraction patterns were obtained for these products, the product of the interaction of iron(II) bromide and potassium amide, and potassium amide. Except for the latter, unsatisfactory patterns resulted from the use of Cu Kα radiation, but satisfactory patterns were obtained using Mo Kα radiation (Zr filter; 80 kv. and 20 ma.; exposure time, 22–24 hr.; samples mounted in thin-walled Pyrex capillaries and rotated at 2 r.p.m.). Typical data are given in Tables II and III.

TABLE II

X-RAY DIFFRACTION DATA

Prod. from $FeBr_2$ + K	Fe^a		Fe_3N^a		Prod. from $FeBr_2$ + KNH_2
d	d	I/I_1	d	I/I_1	d
2.97					2.88
2.54					2.43
2.33			2.38	0.20	
2.19			2.19	0.25	
2.04	2.05	1.00	2.09	1.00	
1.77					1.76
					1.83
1.59			1.61	0.25	
1.47	1.43	0.46			
1.34					
1.29					
1.23			1.24	0.25	1.22
1.16	1.16	0.54	1.16	.20	
			1.14	.10	
1.09			1.09	.03	
			1.04	.05	

[a] Data from A.S.T.M. Index of X-ray diffraction patterns.

TABLE III

X-RAY DIFFRACTION DATA FOR POTASSIUM AMIDE

d	I/I_1	d	I/I_1
3.86	0.09	1.94	0.10
3.53	0.16	1.85	.16
3.01	1.00	1.75	.06
2.71	0.44	1.65	.10
2.43	.13	1.41	.09
2.23	.14	1.34	.05
2.07	.19	1.10	.05

Thermal Decomposition of Reduction Products.—In a typical experiment involving methods described previously,[8] 0.236 g. of a product from the reduction of iron(II) bromide with potassium was heated slowly to 550° and maintained at this temperature for 3 hr. The total volume of gas liberated amounted to 12.4 cc. and was found to consist of 9.9 cc. of nitrogen (4.06×10^{-4} mole), 2.5 cc. of ammonia (1.02×10^{-4} mole), and only traces if any hydrogen. The total nitrogen content of the solid sample calculated on the basis of these data is 5.4%, as compared with the value (Table I) of 5.0% found by direct analysis. In similar experiments equally good or better correlations were obtained in terms of total gases liberated in relation to iron content determinations made before and after thermal decomposition.

Surface Area Measurements.—By a modification[8,9] of the method of Brunauer, Emmett and Teller, the surface area of the product from the reduction of iron(II) bromide with potassium was found to be 8.3 sq. m./g. Electron photomicrographs showed reasonably uniform particle size with an estimated average diameter of 0.1 micron. On the assumption of spherical particles, the calculated surface area is 7.6 sq. m./g.

Catalytic Activity.—As evaluated under conditions described in detail elsewhere,[3] products of the reduction of iron(II) bromide with potassium were found to be entirely inactive as catalysts for the hydrogenation of hexene-1, allyl alcohol and propargyl alcohol. On the other hand, it was observed qualitatively that these products are exceptionally active catalysts for the reaction between potassium and liquid ammonia.[9]

Discussion

The data in Table I show that reduction of iron(II) bromide with potassium yields products in addition to elemental iron and that the gross composition of the ammonia-insoluble reduction products varies over only a fairly narrow range despite considerable variation in the reaction conditions employed.[10] Absence of bromide ion in the insoluble products shows that the conversion of the iron(II) bromide is complete. The most probable interference with complete reduction to elemental iron is the competing interaction of iron(II) bromide and potassium amide resulting from the reaction between potassium and the solvent under the pronounced catalytic influence of iron formed in the primary reduction reaction.

The anticipated initial product of the reaction between iron(II) bromide and potassium amide is iron(II) amide, but if the gross ammonia-insoluble product consisted of elemental iron and iron(II) amide, complete thermal decomposition should yield at least 4 moles of ammonia per mole of nitrogen, providing hydrogen is not formed during the decomposition. The fact that the present experiments showed that thermal decomposition of the reduction products gave 4 moles of nitrogen per mole of ammonia strongly suggested the presence of a nitride, and the presence of Fe_3N was confirmed by the X-ray diffraction data given in Table II. These data show also the presence of elemental iron, one or more products arising from the interaction of iron(II) bromide and potassium amide, and (together with the data of Table III) the absence of potassium amide. The only two diffraction maxima (d = 1.34 and 1.29) not accounted for by the above products do not correspond to any of the lines for possible contaminants such as potassium bromide or potassium hydroxide.

On the basis of information presently available, it has not been found possible to deduce a reasonable mechanism for the formation of Fe_3N. Postulation of a mechanism to account for this product[11] is rendered especially difficult because this substance is not formed in the reaction between the bromide and potassium amide (see Table II). Bergstrom[12] has studied the reaction between iron(II) salts and potassium amide at 25° and his results, although not conclusive, suggested the formation of Fe_3N_2 and an unspecified potassium compound. We were unable to obtain any evidence for the presence of this particular nitride and it appears that the presence of potassium is more likely attributable to the presence of one or more salts of amphoteric bases comparable to those postulated as products of reactions between nickel(II) amide and potassium amide.[3]

AUSTIN, TEXAS RECEIVED FEBRUARY 12, 1951

(8) H. B. Ries, Jr., R. A. Van Nordstrand and W. E. Kreger, THIS JOURNAL, **69**, 35 (1947).

(9) *Cf.* W. M. Burgess and H. L. Kahler, Jr., THIS JOURNAL, **60**, 189 (1938).

(10) In numerous additional experiments for which data are not included here, the iron content of the ammonia-insoluble products was found to range from 79 to 81%.

(11) This nitride has been reported previously as a product of the interaction of an equilibrium mixture of ammonia and hydrogen with iron at 400–440° [S. Brunauer, M. E. Jefferson, P. H. Emmett and S. B. Hendricks, THIS JOURNAL, **53**, 1778 (1931)].

(12) F. W. Bergstrom, *ibid.*, **46**, 2631 (1924).

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[Contribution from the Department of Chemistry, The University of Texas]

An Improved Apparatus for the Study of Reactions in Liquid Ammonia[1,2]

By George W. Watt and C. W. Keenan[3]

Apparatus of the type described by Johnson and Fernelius[4] and modified extensively by Watt and Moore[5] for the conduct of reactions in liquid ammonia at its boiling point involves two serious shortcomings. Neither the original nor the modified apparatus provides for (a) the possibility of conducting titrations in a closed system (a procedure frequently advantageous in establishing the stoichiometry of reactions of liquid ammonia solutions of alkali and alkaline earth metals), or (b) the substantially quantitative removal of solid reaction products following *in situ* filtration and washing, without exposure of these products to the atmosphere. Both of these objectives are realized through use of the apparatus described in the present paper.

Two relatively simple reactions were chosen to demonstrate the operability of the equipment, *i. e.*, the reduction of ammonium bromide and silver(I) bromide with liquid ammonia solutions of potassium.[6] These cases show that the equipment described below permits one to exercise close analytical control over all reactants and products, including gaseous products; the importance of so-doing has been emphasized elsewhere.[7]

Experimental

Apparatus.—The apparatus designed to meet the needs indicated above is shown in Fig. 1. In general, this equipment is similar to that described by Watt and Moore[5]; consequently only the improvements will be pointed out here.

(1) The major part of this work was done under the sponsorship of the Office of Naval Research, Contract N6onr-26610.

(2) The liquid ammonia employed in these studies was generously supplied by E. I. du Pont de Nemours and Company.

(3) Present address: Department of Chemistry, The University of Tennessee, Knoxville, Tennessee.

(4) Johnson and Fernelius, *J. Chem. Education*, **7**, 981 (1930).

(5) Watt and Moore, This Journal, **70**, 1197 (1948).

(6) Several investigators have shown that silver(I) salts other than the bromide are reduced to elemental silver by the action of liquid ammonia solutions of alkali and alkaline earth metals [*cf.*, Kraus and Kurtz, This Journal, **47**, 43 (1925); Burgess and Smoker, *ibid.*, **52**, 3573 (1930); *Chem. Revs.*, **8**, 265 (1931); Zintl, Goubeau and Dullenkopf, *Z. physik. Chem.*, **A154**, 1 (1931); Burgess and Smoker, This Journal, **59**, 459, 465 (1937)].

(7) Fernelius and Watt, *Chem. Revs.*, **20**, 202, 216 (1937).

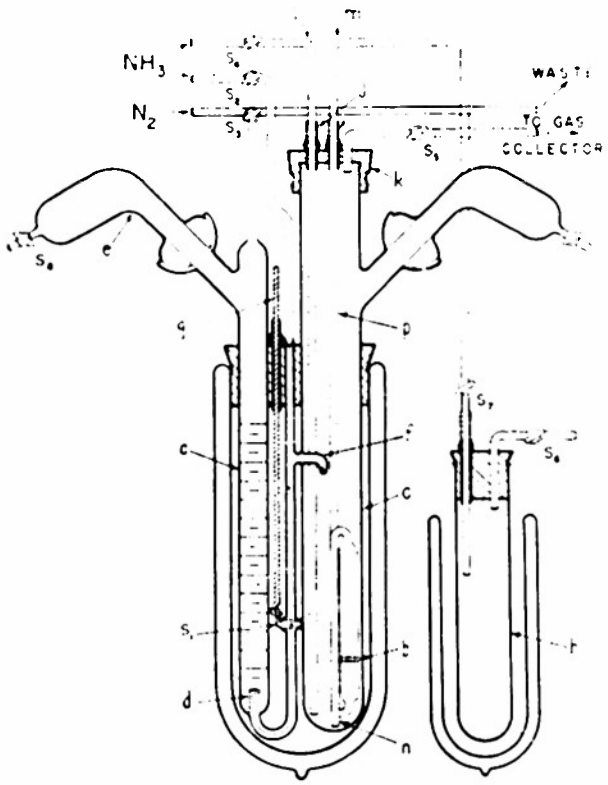

Fig. 1.

The novel features are the buret a and the internal in-line filter[8] b. Both the buret and the main reaction cell c are provided with addition bulbs connected by ball-socket joints held by spring clamps (not shown). In actual operation, ammonia is condensed in the buret until it is approximately one-half full, a known weight of alkali metal[9] is added from tube e, the solution is stirred by a stream of ammonia through the fritted glass filter[10] d, and sufficient additional ammonia is then condensed in a to give a metal solution of the desired concentration. Stopcock s_1 is closed and ammonia is condensed in c, which contains the substance which it is intended to bring into reaction with the metal solution.

Titrations with metal solutions are conducted as follows. With stopcock s_8 open, a positive pressure of dry oxygen-free nitrogen is exerted (through stopcock s_3) upon the surface of the metal solution in a. While the solution (or suspension) in c is stirred by a slow stream of ammonia gas, stopcock s_1 is opened and metal solution is delivered dropwise into c *via* the capillary delivery tip f, and at the same time the metal solution is filtered through d. Addition of metal solution may be interrupted upon the appearance in c of a color change, a precipitate, the beginning or cessation of gas evolution, or the first appearance of the characteristic blue color denoting the presence of excess metal solution.

[Stopcock s_1 is submerged in the coolant ammonia contained in the outer Dewar flask and is lubricated with Dow Corning high vacuum grease. This stopcock is held in place by a spring clamp (not shown) and is manipulated by means of the metal rod g which is connected through a glass ring sealed onto the handle of the stopcock s_1. This rod extends through a glass sleeve in the rubber stopper and the closure between rod and sleeve is made with rubber tubing.]

Upon completion of a reaction that yields a solid product, filtration, washing, and collection of the solid are accomplished as follows. With controlled reduction of the pressure in tube h (evacuated *via* stopcock s_6), stopcock s_7 is opened and the contents of c filtered through b. The solid on the filter b is washed with fresh portions of ammonia successively condensed in c and drawn over through b as described above.[11] At the same time, the filtrate and washings are collected quantitatively in h. *While the solid on the filter is still wet with ammonia*, cap k (together with tubes l, m, and the gas exit tube) is removed from reaction cell c and, with stopcock, s_7 open, a small rubber cap (small bore pressure tubing closed at one end with a screw clamp) is quickly placed over the intake end of the filter tube, *i. e.*, at n. Tube m is then broken off at point p, attached to the vacuum line at point p, evacuated for a few minutes, and sealed off just above n. Following thorough evacuation to remove excess ammonia, tube m is sealed off between p and the top of the filter tube, and transferred to a dry box for all subsequent manipulations. Thus the solid sample is isolated without exposure to the atmosphere.[12]

The cap k is a rubber stopper bored out to fit over the tube c and held firmly in place by a metal collar (not shown) which is tightened with a screw. This type of cap obviates use of a thick stopper which would restrict the side-to-side movement of tubes l and m which are connected through k by means of rubber-to-glass seals which are kept gas-tight by means of spring clamps (not shown).

Titration of Ammonium Bromide Solution with Potassium Solution.—Weighed samples of am-

(8) Ace Glass, Inc., Cat. No. S570, filter tube, porosity C or D.

(9) The metal is cut under dry xylene, so that only freshly cut surfaces are exposed. While still wet with xylene, the metal is transferred to tube e while a current of dry ammonia gas is admitted *via* stopcock s_6. The xylene is volatilized in the ammonia gas stream, tube e is tightly stoppered, stopcock s_6 is closed, and the tube and its contents are weighed. Thereafter, tube e is attached to the side-arm on buret a which is previously flushed out with dry ammonia gas.

(10) Ace Glass, Inc., Cat. No. 8575, filter tube, porosity C.

(11) An alternative procedure is used with very finely divided solids which tend to clog the filter medium. The initial reaction is conducted with filter b raised upward in c so that the intake tip of the filter is above the level of the solution in c. The solid is allowed to settle, filter b is lowered carefully and the supernatant solution is drawn off with minimum disturbance of the settled solid. Thereafter, the solid is washed several times by condensation of fresh ammonia, settling, and decantation, before the bulk of the solid is finally drawn over onto the filter.

(12) While this procedure may appear to involve risk of exposure of the sample to the atmosphere, samples of highly pyrophoric metals which react violently upon the slightest exposure have been handled in this manner without any evidence of atmospheric oxidation.

monium bromide dissolved in approximately 50 ml. of liquid ammonia in c were titrated with potassium solutions of known concentration delivered from the calibrated buret a. The first appearance of a permanent blue color (characteristic of solutions of metals in ammonia) was taken as the end-point. Data for two such titrations are given in Table I (Expts. 1 and 2).

TABLE I

REDUCTION OF AMMONIUM BROMIDE AND SILVER(I) BROMIDE

Expt.	Substance	Reactants, g. Measured	Reactants, g. Calcd.[a]	Products Measured	Products Calcd.[a]	Accted. for, %
	NH_4Br	1.0061				
1	K	0.397[b]	0.402			99
	H_2			109 cc.	115 cc.	95
	NH_4Br	1.0518				
2	K	0.418[b]	.420			100
	H_2			119 cc	120 cc.	99
	AgBr	.3173				
3	K	.0667[b]	.0660			101
	Ag			0.1818 g.	0.1822 g.	99.8
	AgBr	.2877				
4	K	.0598[b]	.0599			100
	Ag			0.1646 g.	0.1653 g.	99.6

[a] Calcd. on the basis of the weight of ammonium bromide or silver(I) bromide used. [b] Measured as a portion (15–20 ml.) of a known volume (25–30 ml.) of potassium solution containing a weighed quantity of potassium.

Reduction of Silver(I) Bromide with Potassium.—Solutions containing known weights of silver(I) bromide were similarly titrated with potassium solutions. In these cases, however, the end-point could not be detected as indicated above, owing to the presence of the black finely divided precipitate of elemental silver. Consequently, a calculated volume of potassium solution was added, the precipitate allowed to settle, and drops of potassium solution were added to the clear supernatant solution until there was no further evidence of reaction. The combined supernatant solution and washings gave a negative test for silver ion. The resulting data are shown as Expts. 3 and 4, Table I.

Summary

An improved apparatus for the conduct of reactions in liquid ammonia at its boiling point has been described, and its utility demonstrated. This apparatus provides for titrations employing liquid ammonia solutions of metals and permits one to carry out filtration and purification operations at the boiling point of the solvent.

It has been demonstrated that silver(I) bromide is reduced to elemental silver by reaction with solutions of potassium in liquid ammonia.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TEXAS]

The Reduction of Certain Cobalt Salts in Liquid Ammonia[1]

BY GEORGE W. WATT AND C. W. KEENAN

Data are given to show that, in reaction with potassium in liquid ammonia, cobalt(II) nitrate is converted to cobalt(II) amide, with concomitant reduction of nitrate to nitrite. Cobalt(II) amide and cobalt(III) bromide are reduced principally to elemental cobalt. Data on the comparative activity of this product as a hydrogenation catalyst are included.

The reduction of salts of nickel and iron to the corresponding metals (and other products) by means of liquid ammonia solutions of potassium, and results obtained in the use of these reduction products as catalysts for the hydrogenation of certain olefins have been described in earlier papers from these laboratories.[2,3] The present paper is concerned with similar data relating to cobalt.

Experimental

With the exceptions noted below, all experimental methods and materials were the same as those described previously.[2,3]

Cobalt(II) nitrate 6-ammonate was prepared by a minor modification of the method of Ephraim and Rosenberg.[4] The ammonia content of this salt was found to be extremely sensitive to the temperature employed during its formation.

Anal. Calcd. for $Co(NO_3)_2 \cdot 6NH_3$: Co, 20.7; NH_3, 35.8. Found: Co, 20.6; NH_3, 37.0.

Cobalt(III) bromide 6-ammonate was prepared as directed by Bjerrum.[5]

Anal. Calcd. for $CoBr_3 \cdot 6NH_3$: Co, 14.7; Br, 59.9. Found: Co, 14.7; Br, 60.0.

Cobalt for use in comparative studies of catalytic activity and related properties was prepared by reducing cobalt(III) oxide with hydrogen[6] for 22 hr. at 250–260°.

Anal. Found: Co, 100.3.

Reduction of Cobalt(II) Nitrate 6-Ammonate.—In a typical experiment, a *solution* of 1.345 g. of cobalt(II) nitrate 6-ammonate in 65 ml. of liquid ammonia at −33.5° was titrated with 0.544 *M* potassium solution[7] until a total of 0.372 g. of the metal had been added [mole ratio $K/Co(NO_3)_2 = 2.02$]. Throughout the course of the reaction a bulky blue precipitate was formed; *there was no liberation of hydrogen* or other insoluble gas, and the supernatant solution was colorless. The precipitate was washed with liquid ammonia and dried *in vacuo* at room temperature for 3 hr., during which the solid gradually became black. This product was at no time exposed to the atmosphere.

Anal. Calcd. for $Co(NH_2)_2$: Co, 64.8. Found: Co, 65.4.

The solid residue remaining after evaporation of the combined filtrate and washings was dissolved in water to form a colorless solution which gave positive tests for nitrite ion (aniline–phenol test) and nitrate ion [brucine–tin(II) chloride test].

Reduction of Cobalt(II) Amide.—Cobalt(II) nitrate 6-ammonate (0.711 g.) was converted to cobalt(II) amide in the manner described above. The amide was washed thoroughly, resuspended in 60 ml. of liquid ammonia and treated with a volume of standard potassium solution approximately 15% in excess of that calculated for reduction of the amide to elemental cobalt. The resulting black solid was washed with ammonia and dried *in vacuo* at room temperature. The resulting solid was found to contain only 90.1% cobalt, and in no case was cobalt(II) amide reduced to a product of higher cobalt content. Largely because of the unattractive physical properties of cobalt(II) amide and the difficulties attendant upon handling this intermediate in the available equipment, neither cobalt(II) nitrate nor cobalt(II) amide was investigated further.

Reduction of Cobalt(III) Bromide 6-Ammonate.—Suspensions of this salt in *ca.* 65 ml. of liquid ammonia were reduced with potassium added both as solid and in liquid ammonia solution. In either case the bromide was rapidly converted to a black solid, hydrogen was evolved throughout the course of the reaction, and blue-green and red colored solutions were formed depending upon the rate of addition of potassium. Upon completion of the reactions, the insoluble products were washed with ammonia, dried *in vacuo* at room temperature, and at all times protected from the atmosphere since these products were markedly pyrophoric. Solutions of these products in dilute nitric acid did not give positive tests for bromide ion. Representative data that show the effect of variation of reaction ratios and mode of addition of potassium upon the cobalt content of the ammonia-insoluble products are given in Table I, which also includes information relative to different modes of treatment of these products.

TABLE I

REDUCTION OF COBALT(III) BROMIDE WITH POTASSIUM IN LIQUID AMMONIA

Run No.	Salt, g.[a]	K, g.	K/$CoBr_3$	Co, %[b]
13	6.789	2.550[c]	3.85	90.8[d]
14	3.398	2.749	8.29	92.6[e]
15	3.422	3.508[c]	10.5	87.0
16	3.398	2.456	7.41	96.1
18	3.401	2.407	7.26	96.6
19	3.406	2.364	7.12	90.8[f]
21	3.401	2.156	6.50	93.4[g]

[a] Added in the form of $CoBr_3 \cdot 6NH_3$. [b] The cobalt content of fourteen independent reduction products ranged from 86.2 to 96.6%; average, 92.4. [c] Potassium added in liquid ammonia solution. [d] Found: NH_3, 3.8; K, 3.3; total accounted for, 97.9. [e] Found: NH_3, 1.1; K, 6.0; total accounted for, 99.7. [f] Ammonia-insoluble product was washed, resuspended in liquid ammonia, and treated with 1.201 g. of ammonium bromide. [g] After washing with ammonia, the insoluble product was removed from the reactor as a slurry in absolute ethanol.

X-Ray Diffraction Patterns.—The presence of elemental cobalt in the products of the reduction of cobalt(III) bromide with potassium in ammonia and of cobalt(III) oxide with hydrogen was established by means of X-ray powder-diffraction patterns using samples mounted in Pyrex capillary tubes. The data are given in Table II; no extraneous lines were observed.

Surface Area Measurements.—By means of a modification[8] of the method of Brunauer, Emmett and Teller, the surface area of cobalt from cobalt(III) bromide was found to be 24 $m.^2/g.$ Similarly, the area found for cobalt from cobalt(III) oxide was 2 $m.^2/g.$ On the basis of electron photomicrographs obtained through the use of an RCA Type EMU-1 electron microscope,[9] the average particle diameters for cobalt from the oxide and bromide were estimated to be 2.5 and 0.01 micron, respectively. If spherical particles are assumed, the corresponding calculated areas are 1.3×10^{-2} and 8.4 $m.^2/g.$, respectively. This marked divergence

(1) This work was supported, in part, by the Office of Naval Research, Contract N6onr-26610.

(2) G. W. Watt, W. P. Roper and S. G. Parker, THIS JOURNAL, 73, 5701 (1951).

(3) G. W. Watt and W. A. Jenkins, Jr., *ibid.*, 73, 3275 (1951).

(4) F. Ephraim and E. Rosenberg, *Ber.*, 51, 130 (1918).

(5) J. Bjerrum, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 219.

(6) H. Moissan, *Ann. chim. phys.*, 21, 242 (1880).

(7) Identical results were obtained in experiments in which the potassium was added as a solid

(8) H. E. Ries, Jr., R. A. Van Nordstrand and W. E. Kreger, THIS JOURNAL, 69, 35 (1947).

(9) The assistance of L. L. Ames is gratefully acknowledged.

TABLE II

X-RAY DIFFRACTION DATA FOR COBALT

Co[a]		Co from $CoBr_2$[b]		Co from Co_3O_4[c]	
d	I/I_1	d	Relative intensity	d	Relative intensity
2.158	0.25	2.17	Weak	2.15	Weak
2.037	1.0	2.03	Strong	2.02	Strong
1.915	1.0	1.91	Strong	1.90	Strong
1.773	0.15	1.76	Weak	1.79	Weak
1.484	.03	1.50	Weak		
1.250	.5	1.26	Weak	1.25	Weak
1.148	.1	1.14	Weak		
1.066	.6	1.06	Medium	1.06	Medium
1.045	.5			1.04	Weak

[a] Data from A.S.T.M. Index of X-Ray Diffraction Patterns. [b] MoKα, Zr filter; 25 hr. exposure at 80 kv. and 20 ma. [c] CuKα, Ni filter; 23 hr. exposure at 80 kv. and 18 ma.

between the measured and estimated values suggests that both cobalt samples were of quite porous structure.

Determination of Adsorbed Hydrogen.—In the manner described previously[9] samples of the ammonia-insoluble product from the reduction of cobalt(III) bromide were heated at temperatures up to 600° for as much as 17 hr. The hydrogen evolved amounted to an average of 7.1 cc./g. In one case (Table 1, Run 19), the hydrogen liberated upon treatment of the ammonia-insoluble product with ammonium bromide in liquid ammonia was measured and found to amount to 6.4 cc./g.

Catalytic Activity.—All evaluations of catalytic activity of cobalt were made using methods and conditions described previously,[9] with the exception that cobalt catalysts were of the order of 0.2 g. and the duration of pre-treatment with hydrogen was one hour.[10]

Although cobalt produced by the reduction of cobalt(III) oxide with hydrogen was found to be entirely inactive as a catalyst for the hydrogenation of allyl alcohol at 30° and 1500 mm. hydrogen pressure, cobalt from the reduction of cobalt(III) bromide in liquid ammonia was active but somewhat less so than Raney nickel. The typical data shown in Fig. 1 illustrate the reproducibility of the catalysis prepared in ammonia (Runs 16 and 18), and the effect of pre-treatment with ammonium bromide (Run 19) and ethanol (Run 21). Rate data for Raney nickel W-6 are included for comparison.

Discussion

The products of the reduction of cobalt(II) nitrate with two atomic equivalents of potassium in liquid ammonia have been shown to consist of insoluble cobalt(II) amide and a mixture of soluble nitrate and nitrite ions. It is difficult to account for these products since hydrogen was not liberated and because potassium hydroxide was not present as an insoluble product at the end of the reactions. The following equations are compatible with the observed facts

$$Co(NO_3)_2 + 2K \longrightarrow Co(NO_3)(NO_2) + K_2O \quad (1)$$

$$K_2O + NH_3 \longrightarrow KOH + KNH_2 \quad (2)$$

$$Co(NO_3)(NO_2) + KNH_2 \longrightarrow Co(NO_2)(NH_3) + KNO_3 \quad (3)$$

$$Co(NO_3)(NH_3) + KOH + NH_3 \longrightarrow Co(NH_3)_3 + KNO_2 + H_2O \quad (4)$$

The cobalt(II) amide produced in these reactions is identical in physical properties to that produced by Bergstrom[11] by the interaction of cobalt(II) thiocyanate and potassium amide in liquid ammonia. The reduction of nitrate to nitrite by solutions of metals in ammonia has been observed previously,[12,13] and equation (2) represents a well known reaction.[14]

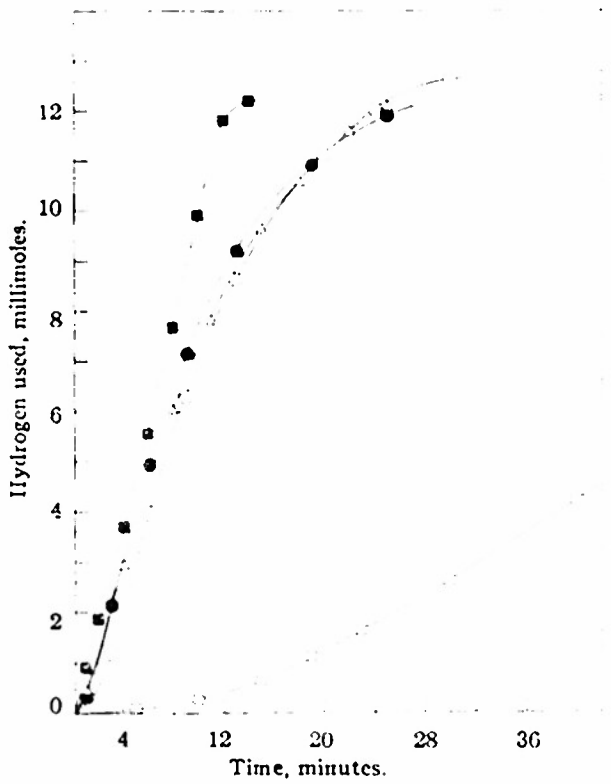

Fig. 1.—Hydrogenation of allyl alcohol over cobalt catalysts: O, Co, 0.196 g., run no. 16; ●, Co, 0.203 g., run no. 18; ⊙, Co, 0.139 g., run no. 19; △, Co, 0.205 g., run no. 21; ■, Raney Ni, 0.0206 g.

When, in an effort to reduce the cobalt(II) amide to elemental cobalt, excess potassium (as much as seven atomic equivalents) is added, substantially all of the nitrate ion is reduced to nitrite, and the ammonia-insoluble product consists principally of potassium hydroxide and elemental cobalt together with small quantities of impurities containing cobalt, nitrogen and potassium. Variable quantities of hydrogen are liberated (owing to conversion of excess potassium to potassium amide under the catalytic influence of the elemental cobalt). These products may be accounted for by reactions occurring subsequent to those represented by equations (1) to (4) or by the equations

$$Co(NO_3)_2 + 4K \longrightarrow Co(NO_2)_2 + 2K_2O \quad (5)$$

$$2K_2O + 2NH_3 \longrightarrow 2KOH + 2KNH_2 \quad (6)$$

$$Co(NO_2)_2 + 2KNH_2 \longrightarrow Co(NH_3)_2 + 2KNO_2 \quad (7)$$

$$Co(NH_3)_2 + 2K \longrightarrow Co + 2KNH_2 \quad (8)$$

Except for the formation of small quantities of by-products containing potassium and nitrogen, the reduction of cobalt(III) bromide with potassium produces principally elemental cobalt. In contrast to cobalt formed by reduction of cobalt(III) oxide with hydrogen, the product from the bromide exhibits marked activity as a catalyst for the hydrogenation of allyl alcohol at room tem-

(10) The pre-treatment was extended from 15 min. to 1 hr. to eliminate an induction period more pronounced in the case of cobalt than previously observed in studies involving nickel.[9]

(11) P. W. Bergstrom, THIS JOURNAL, 46, 2631 (1924).

(12) W. M. Burgess and F. R. Holden, *ibid.*, 59, 461 (1937).

(13) F. W. Bergstrom, *ibid.*, 62, 2381 (1940).

(14) C. A. Kraus and E. F. Whyte, *ibid.*, 48, 1781 (1926).

perature and a hydrogen pressure of two atmospheres. The catalytic activity is quite reproducible despite considerable variation in the cobalt content of the ammonia-insoluble product. These catalysts are largely deactivated by treatment with ammonium bromide (an acid) in liquid ammonia and it is of interest to note that the quantity of hydrogen thereby liberated is in good agreement with that obtained by thermal desorption. These catalysts are also somewhat deactivated by *extensive* washing with, or long periods of storage under, absolute ethanol, although as shown in Fig. 1 (Run 21) their activity is substantially uninfluenced by limited exposure to ethanol. Preliminary studies of the kinetics of the hydrogenation reaction indicate that it is first order with respect to the concentration of allyl alcohol. The significance of this fact, as well as the surface area data, will be considered in later papers concerned with other transitional metal catalysts formed by the reduction of salts in liquid ammonia.

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The Composition of W-6 Raney Nickel[1]

By George W. Watt and Sidney G. Parker[2]

In a recent note, Ipatieff and Pines[3] published data on the composition of W-6 Raney nickel that differ markedly from results given earlier by Adkins and Billica[4] and from data obtained by the present authors prior to the appearance of the note by Ipatieff and Pines. The latter authors *assumed* that a nitric acid-insoluble residue obtained during the preparation of samples for analysis consisted of aluminum(III) oxide and that sodium was present as a sodium aluminate. Of the total aluminum found, one fraction was calculated as sodium aluminate on the basis of sodium found by analysis, another small fraction was attributed to elemental aluminum, while the major portion was interpreted as being present as aluminum(III) oxide, presumably in order that the sum of the various constituents be made exactly equal to 100%. No consideration was given to the presence of minor constituents other than sodium, and Ipatieff and Pines concluded that the aluminum(III) oxide is present in the catalyst formed by the method of Adkins and Billica[4] and influences the activity of the catalyst.

Following publication of the note by Ipatieff and Pines, we repeated most of our experiments and confirmed the results obtained earlier. The catalysts used in our work were prepared exactly as described by Adkins and Billica; with one exception, the method of preparation of samples for analysis and the analytical procedures for the determination of nickel and aluminum were identical with those specified by Ipatieff and Pines. In contrast to the work of the latter authors, however, the nitric acid-insoluble residue was separated by filtration, washed with water, dried, and weighed; the filtrates were analyzed for aluminum.[5] Whereas Ipatieff and Pines describe the nitric acid-insoluble residue as a dense white solid, we found a grayish-white residue sufficient only to impart a pronounced turbidity to the nitric acid solution. Data relative to the aluminum content of these catalysts are given in Table I; the identity of the nitric acid-insoluble residue as $Al_2O_3 \cdot 3H_2O$ is established by the X-ray diffraction data given in Table II.

Table I

Aluminum Content of W-6 Raney Nickel

[a] HNO_3, %	$Al_2O_3 \cdot 3H_2O$, %	Al, %
5	1.0	12.2
10	1.0	12.5
30	0.4	12.9
60	0.5	13.0

[a] Concentration of acid used to dissolve samples for analysis.

Table II

X-Ray Diffraction Data for Aluminum(III) Oxide 3-Hydrate[a]

[b] HNO_3 insol. residue		[c] α-$Al_2O_3 \cdot 3H_2O$	
D, Å.	*I*/*I*$_1$	*D*, Å.	*I*/*I*$_1$
4.73	0.9	4.85	1.00
4.40	.7	4.37	.84
3.22	.5	..	..
..	..	2.46	.59
2.07	1.0	2.38	.59
..	0.2	2.05	.41
1.71	.7	1.75	.41
1.60	.2	1.69	.41
1.45	.2	1.46	.41
1.39	.2	1.41	.31

[a] Although more complete data are available, only the ten most intense diffraction maxima are included here. [b] Data obtained using Cu K_α radiation, Ni filter, 2–3 hr. exposure at 30 kv. and 15 ma.; samples mounted in cellulose acetate capillary tubes. [c] Data from A.S.T.M. Index of X-Ray Diffraction Patterns.

Spectrographic analysis of nitric acid solutions of independent samples of W-6 Raney nickel[6] for minor constituents gave the following results (in per cent.): Na (0.5); Fe, Cu (0.2); Ca (0.1); Mg (0.005); <2: Ce, Hg; <0.2: Ba, Cd, Co, Cr, In, La, Li, Mn, Pb, Sr, Ti, Zn, Zr. Elements not detected include Ag, As, Au, Bi, Ga, K, Mo, P, Pt, Sb, Sn, Th, Tl, U, V, and W; C was not detected owing to interference.[7] The elements detected spectrographically, together with hydrogen and oxygen, presumably account for that fraction

(1) This work was supported, in part, by the Office of Naval Research, Contract N6onr-26610.

(2) Field Research Laboratories, Magnolia Petroleum Company, Dallas, Texas.

(3) V. N. Ipatieff and H. Pines, This Journal, **72**, 5320 (1950).

(4) H. Adkins and H. R. Billica, *ibid.*, **70**, 695 (1948).

(5) The nickel content of these particular catalyst samples was 80.2%. In other cases, nickel contents as low as 70–75%, with correspondingly high aluminum content (11–15%) were found depending upon the conditions employed in the preparation of the catalysts.

(6) The writers are indebted to Dr. W. W. Marshall through whose cooperation these data were obtained.

(7) The following data (in per cent.) were obtained for independent samples of commercial Raney alloy: Ni (49.5), Al (49.8); <0.2: As, Ce, Cu, Hg, U; <0.1: Ba, In, Pb, Sb, Th, Zn; <0.05: Cd, Fe, Sn; <0.01: Bi, Ca, Co, Cr, La, Li, Mg, Mn, Na, Nb, Sr, Ti, V, Zr.

of the catalyst not represented by nickel and aluminum. The spectrographic analysis for sodium is in good agreement with results of chemical analyses; this element may be present as sodium aluminate[3] or as sodium hydroxide not removed despite extensive washing.

The data given in Table I show that the maximum alumina formed is 1% rather than 21% as reported by Ipatieff and Pines. Since aluminum (III) oxide is insoluble in hot 60% nitric acid, the small but measurable difference in the quantity of alumina found using concentrated and dilute acid cannot be attributed to solubility. Furthermore it is significant that the decrease in the quantity of alumina found when concentrated nitric acid is used to dissolve the catalyst samples parallels qualitatively the trend in oxidation potential of nitric acid as a function of concentration. This clearly indicates that alumina is not a constituent of W-6 Raney nickel prepared by the method of Adkins and Billica but rather that alumina is formed during dissolution of the samples taken for analysis. This conclusion is further supported by X-ray diffraction studies on Raney nickel carried out both in this laboratory and in connection with work described by Taylor and Weiss.[8] In both instances, no diffraction maxima attributable to any of the known forms of aluminum(III) oxide or its hydrates were observed. Finally, it should be recognized that the type of specific composition data proposed by Ipatieff and Pines is also unwarranted on the grounds that, even with respect to the two major components, the composition of W-6 Raney nickel catalysts is not rigorously reproducible and varies over an appreciable range owing to unavoidable variation in the conditions that prevail during the leaching of the nickel-aluminum alloy.

8) A. Taylor and J. Weiss, *Nature*, **141**, 1055 (1938).

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[Contribution from the Department of Chemistry of the University of Texas]

The Catalytic Activity of Metals Produced by the Reduction of Salts in Liquid Ammonia. II. Nickel[1]

By George W. Watt, Wilbur F. Roper[2] and Sidney G. Parker[2]

Studies on the preparation and properties of nickel hydrogenation catalysts formed by the reduction of nickel(II) bromide with potassium in liquid ammonia show that the ammonia-insoluble reduction products include (in addition to elemental nickel and nickel amide) a potassium-containing substance that reacts with ethanol (the hydrogenation reaction medium) and with allyl alcohol (one of the hydrogen acceptors employed) and influences both the rate and mechanism of the hydrogenation of the latter.

It was reported earlier[3] that nickel from the reduction of nickel(II) bromide with potassium in liquid ammonia exhibits appreciable activity as a catalyst for the hydrogenation of allyl alcohol. More detailed studies are described in the present paper. Catalysts prepared in liquid ammonia, W-6 Raney nickel, and nickel from the reduction of nickel(II) oxide with hydrogen are compared in terms of surface areas, adsorbed hydrogen and hydrogenation rate measurements.

Experimental

Materials.—Nickel(II) bromide 6-ammonate was prepared as described by Watt.[4] Allyl alcohol was generously supplied by the Shell Chemical Corporation. Physical constants found (literature[5] values in parentheses): b.p. 96.7–96.9° cor. (96.90–96.98°); $n^{25}D$ 1.4108 (1.4111). Hexene-1 (research grade, purity 99.22 ± 0.10%) obtained from the Phillips Petroleum Co. was used without further purification.

Preparation of Nickel Catalysts.—W-6 Raney nickel was prepared as described by Adkins and Billica,[6,7] stored under absolute ethanol at 0°, and at all times protected from the atmosphere.

Nickel was prepared from nickel(II) oxide by reduction with predried hydrogen[8] at known temperatures within the range 265–310°, cooled to room temperature in an atmosphere of dry hydrogen, and thereafter protected from exposure to the atmosphere. The nickel content of these products ranged from 96.0 to 97.5%.

The preparation of nickel catalysts by the reduction of nickel(II) bromide (used in the form of the 6-ammonate) with solutions of potassium in liquid ammonia was carried out using equipment and procedures described elsewhere.[9,10] Variables in addition to those investigated previously[3] were studied in an effort to produce catalysts having a nickel content comparable to those from the reduction of nickel(II) oxide with hydrogen. From runs employing from 1.5 to 3.0 g. of nickel(II) bromide 6-ammonate dissolved and suspended in from 12 to 65 ml. of liquid ammonia, and reduction with 2 to 4 gram atoms of potassium/mole of bromide, ammonia-insoluble products having a wide range of composition were obtained, *i.e.*, Ni, 47–90%; N, 2–13% and K, 10–28%. In 10 runs for which complete analytical data are available, analyses for these three elements account for an average of 94% of the gross ammonia-insoluble product. In addition to the range of variables indicated above, frequency of agitation and repetition of addition of potassium were also studied. In the latter experiments, the initial solid reduction products were washed with liquid ammonia, resuspended in ammonia and treated with excess potassium in an unsuccessful effort to reduce the by-product nickel(II) amide to elemental nickel.[11] The product of highest nickel content (90%) was obtained by reducing 2.0 g. of the bromide in 12 ml. of ammonia with 0.75 g. of potassium; the solid product was washed seventeen times with 20-ml. portions of ammonia. All transfers of solid catalyst samples were made in an inert oxygen-free atmosphere in a dry-box.

Surface Area Measurements.—Surface areas were measured by a modification[12] of the method of Brunauer, Emmett and Teller. Values found for nickel prepared in liquid ammonia ranged from 5 $m.^2/g.$ for a product containing 67% Ni to 8 $m.^2/g.$ for one containing 84% Ni. Simi-

(1) This work was supported, in part, by the Office of Naval Research, Contract N6onr-26610.

(2) Field Research Laboratories, Magnolia Petroleum Co., Dallas, Texas.

(3) G. W. Watt and D. D. Davies, This Journal, **70**, 3753 (1948).

(4) G. W. Watt, *Inorganic Syntheses*, **3**, 194 (1950).

(5) Shell Chemical Corporation, "Allyl Alcohol," Tech. Publication 40-22, Knight-Counihan Co., San Francisco, p. 42, 1946.

(6) H. Adkins and H. R. Billica, This Journal, **70**, 695 (1948).

(7) Data on the composition of W-6 Raney nickel catalysts will be published elsewhere.

(8) V. Ipatieff, *J. prakt. Chem.*, **77**, 513 (1908).

(9) G. W. Watt and T. E. Moore, This Journal, **70**, 1197 (1948).

(10) G. W. Watt and C. W. Keenan, *ibid.*, **71**, 3833 (1949).

(11) W. M. Burgess and J. W. Eastes, *ibid.*, **63**, 2674 (1941).

(12) H. B. Ries, R. A. Van Nordstrand and W. E. Kreger, *ibid.*, **69**, 35 (1947).

larly, the area of nickel from nickel(II) oxide was found to be 17 m.²/g., while that of W-6 Raney nickel was 87 m.²/g.

Measurement of Adsorbed Hydrogen.—Hydrogen adsorbed on or otherwise associated with the nickel catalysts was measured as follows. Samples contained in an especially designed Pyrex glass sample tube attached to a Toepler pump were heated to known temperatures as high as 550°, or until gas evolution ceased. The gas was pumped off and collected over mercury in a gas buret attached to a gas analysis train. Reduction products of nickel(II) bromide having widely different compositions yielded from traces up to 29 cc. H_2/g., 26.83 cc. NH_3/g. and 2–34 cc. N_2/g. Under identical conditions nickel from nickel(II) oxide yielded no hydrogen over periods up to 8 hr. W-6 Raney nickel that had aged 2 to 12 months gave 40 to 74 cc. H_2/g.; the average was 59 cc./g.

Catalytic Activity.—The activity of the three different types of nickel catalysts was evaluated in terms of the rate of hydrogenation of allyl alcohol using a modification of the apparatus described by Joshel.[13] Practically all rate data were obtained using 14.63 millimoles of allyl alcohol (0.850 g.) in 10.0 ml. of absolute ethanol at 30.0 ± 0.5°, at a hydrogen pressure of 1500 ± 5 mm., and with agitation at a frequency of 930 r.p.m. To eliminate induction periods, catalysts prepared in ammonia were pretreated with hydrogen for 15 min. prior to introduction of the acceptor; nickel from nickel(II) oxide[14] was similarly pretreated for 30 min.

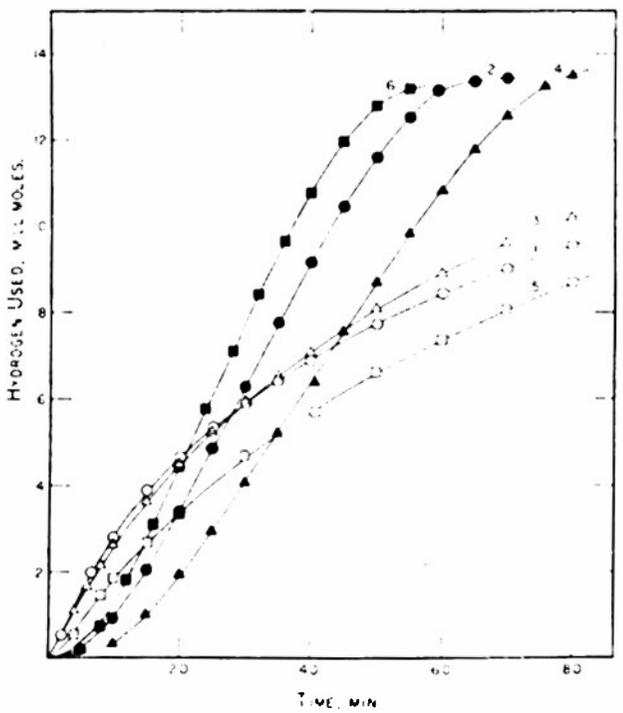

Fig. 1.—Hydrogenation of allyl alcohol over Ni from $NiBr_2$: ○, raw catalyst; ●, washed; △, KOC_2H_5 added; ▲, washed; □, KOH added; ■, washed, 40°.

(13) L. M. Joshel, *Ind. Eng. Chem., Anal. Ed.*, **15**, 590 (1943). Although designed for analytical purposes, this equipment has been found adaptable to the procurement of reliable rate data. In preliminary studies with W-6 Raney nickel, the maintenance of steady state conditions over at least 75% of the total reaction time was demonstrated repeatedly. Variables investigated included temperature, hydrogen pressure, agitation frequency, ratio of catalyst to acceptor and acceptor to solvent, concentration of the hydrogenation product, and age of the catalyst. That these studies led to substantially the same conclusions reached by others [see, for example, (a) J. Bougault, E. Cattelain and P. Chabrier, *Bull. soc. chim.*, [5] **5**, 1699 (1938); (b) H. A. Smith, W. C. Bedoit and J. F. Fuzek, THIS JOURNAL, **68**, 229 (1946)] who used other types of equipment serves further to establish the reliability of the methods employed in the present work.

(14) These products were found to be totally inactive as catalysts for the hydrogenation of allyl alcohol when the oxide was reduced at 300–310°. Catalysts reproducible with respect to both composition and activity result when the oxide is reduced at 265–285°; *cf.* Ipatieff and Kelber [*Ber.*, **49**, 55 (1916)].

Data which show that the catalytic activity of nickel from nickel(II) bromide is essentially independent of the composition of the ammonia-insoluble reduction product are given in Table I. These data show also the extent of purification accomplished by washing with ethanol; attempts to identify the impurities thereby removed, by means of X-ray diffraction patterns, were unsuccessful.

The rate of hydrogenation of allyl alcohol over nickel prepared in liquid ammonia is shown for a typical case by curve 1 in Fig. 1. In this run, 0.120 g. of a catalyst containing 66.6% Ni, 6.3% N, and 22.9% K was used. Upon completion of the hydrogenation, the nickel was held at the bottom of the flask with the stirrer magnet and the solution and suspension of impurities was drawn off under conditions that obviated exposure to the atmosphere. The catalyst was then washed 8 times with 10-ml. portions of absolute ethanol and subsequently used for the run shown as curve 2. In an effort to reproduce the rate behavior characteristic of the raw catalyst, the nickel was again washed as described above and used for another hydrogenation after addition of potassium ethoxide at a concentration equivalent to the potassium content of the raw catalyst (curve 3, Fig. 1). The potassium ethoxide was then washed out with ethanol and the washed catalyst was used in the run represented by curve 4. The above sequence was repeated using potassium hydroxide in place of potassium ethoxide (curve 5). Finally, the potassium hydroxide was removed by washing with ethanol and the washed catalyst was used for a hydrogenation at 40° (curve 6). The catalyst finally recovered weighed 0.060 g. and contained 98.0% Ni; the loss in weight includes both impurities and elemental nickel unavoidably lost during the many washing operations.

TABLE I

COMPOSITION AND ACTIVITY OF CATALYSTS PREPARED IN LIQUID AMMONIA

Catalyst [a] wt., mg.	Nickel content, % [b] Raw catalyst	[c] After use	[d] $(\Delta m/\Delta t)$
81	71.3	..	0.14
94	57.0[e]	..	.14
96	79.6	..	.14
88	75.0	95.5	.17
90	86.6	96.0	.18
67	90.5	96.2	.16
60	66.6[e]	98.0	.11

[a] Weight determined after use in hydrogenation runs. In most cases the weights of raw catalysts were known and the decrease in weight occasioned by washing with ethanol (see footnote *e*) paralleled closely the composition of the raw catalyst. Thus, about 60 mg. was lost in washing the raw catalyst that contained 66.6% Ni, while only 14 mg. was removed from that containing 90.5% Ni. [b] *I.e.*, the ammonia-insoluble reduction product sampled without exposure to the atmosphere or to absolute ethanol. [c] Catalyst washed with *cc.* 80 ml. of absolute ethanol. [d] Values in terms of millimoles of hydrogen consumed/min., after reaction had proceeded for 30 min. [e] In cases involving reduction products of low elemental nickel content, there was visual evidence of reaction upon contact with absolute ethanol.

The above results indicate that the raw catalyst contains an impurity which solvolyzes upon contact with ethanol to form potassium ethoxide. Such an impurity could similarly give rise to the potassium salt of allyl alcohol, thereby altering diffusion rate, adsorption characteristics, or other rate-controlling steps involving the hydrogen acceptor. Accordingly, hydrogenation runs using 1.346 g. (0.016 mole) of hexene-1, an acceptor not susceptible to the complications suggested above, were made under conditions already specified. The data shown in Fig. 2 support the assumptions made with reference to the nature of the impurity in the raw catalysts.

A comparison of the rates of hydrogenation of allyl alcohol over W-6 Raney nickel, nickel from nickel(II) oxide, and nickel from the reduction of nickel(II) bromide with potassium in liquid ammonia is shown in Fig. 3.

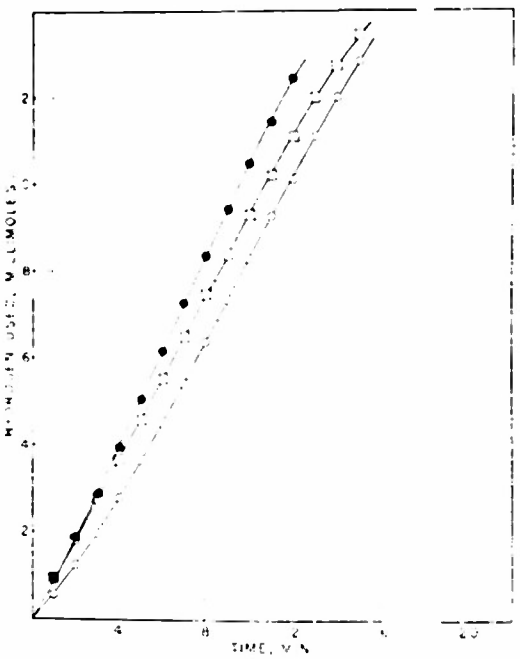

Fig. 2.—Hydrogenation of hexene-1 over Ni from $NiBr_2$: ●, raw catalyst; □, KOC_2H_5 added; ○, washed.

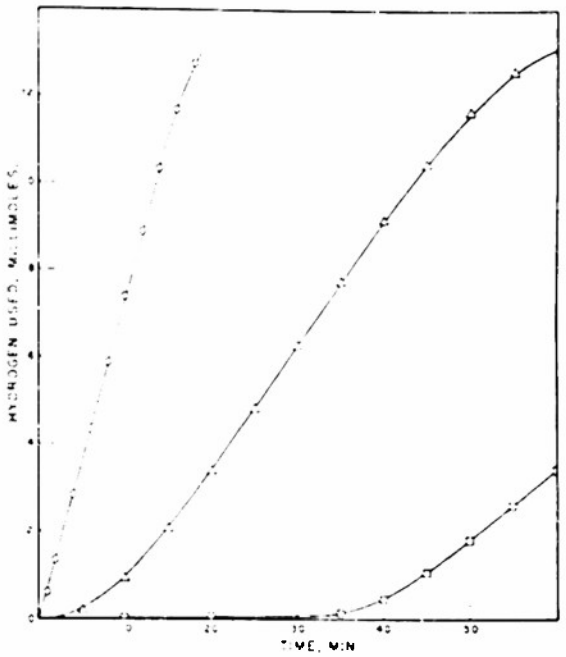

Fig. 3. Comparative activity of nickel catalysts for the hydrogenation of allyl alcohol: □, Ni from NiO; △, Ni from $NiBr_2$; ○, W 6 Raney Ni.

Discussion

Work described in this paper and elsewhere[3] shows that the reduction of nickel(II) bromide with ammonia solutions of potassium results in the formation of elemental nickel, nickel(II) amide 2-ammonate, and one or more potassium-containing products. The latter might be expected to result from the action of potassium amide upon nickel (II) amide and/or its deammoniation products, thereby giving rise to ammonia-insoluble salts of amphoteric bases such as that described by Bohart,[15] *i.e.*, $KN(NiNK_2)_2 \cdot 6NH_3$. Data obtained by analysis of the ammonia-insoluble reduction products however fail to show a constant ratio of potassium to nitrogen and indicate that more than one such by-product is formed. The isolation of these substances presents an especially difficult problem and we have been unable either to effect a separation or to obtain X-ray diffraction patterns that might serve as a basis for identification.

The heats of activation calculated by the Arrhenius equation for hydrogenations of allyl alcohol over two independent samples of catalysts prepared in liquid ammonia are 10 and 7 kcal./mole. The surface areas of W-6 Raney nickel found in this work are somewhat higher than those found by Smith and Fuzek[16] who used data on the adsorption of palmitic acid from benzene solutions. Ammonia adsorption should lead to higher areas owing to the presence of surface less readily accessible to the larger palmitic acid molecules. Also, Ries, *et al.*,[12] reported that ammonia adsorption gave somewhat higher surface area values than nitrogen adsorption. Finally, it should be recognized that the difference between the quantity of adsorbed hydrogen found on Raney nickel in the present work (59 cc./g.) and that reported by Bougault, *et al.*,[13a] is reasonable in view of the difference in the age of the samples employed.

AUSTIN, TEXAS RECEIVED FEBRUARY 2, 1951

(15) G. S. Bohart, *J. Phys. Chem.*, **19**, 537 (1915).

(16) H. A. Smith and J. F. Fuzek, THIS JOURNAL, **68**, 229 (1946).

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The Relative Catalytic Activity of Nickel Produced by the Reduction of Nickel(II) Bromide with Liquid Ammonia Solutions of Different Alkali Metals[1]

By George W. Watt and Peggy I. Mayfield

Received November 1, 1952

Burgess and co-workers have reported marked differences in both the chemical and catalytic activity of silver and nickel precipitated by the reduction of salts with solutions of metals in liquid ammonia at its normal boiling temperature. Thus, the reduction of certain silver salts with solutions of potassium yielded silver far more active than that which resulted when sodium was employed.[2] Similar differences were observed in studies involving the reduction of silver salts with solutions of calcium[3] and in the reduction of nickel salts with sodium, potassium and calcium.[4] No explanation of these differences was proposed by Burgess, *et al.*, and since similar observations have been made in our laboratories it seemed worthwhile to carry out somewhat more definitive experiments.

In view of the presently accepted interpretation of the physical nature of solutions of metals in liquid ammonia,[5] it seems unlikely that differences in the properties of these reduction products are attributable to any inherent differences in the nature of the metal solutions. Rather it is more likely that both the chemical and catalytic activities of the reduction products are determined by rate factors and solubility relationships.

Although both the rates of solution of the alkali and alkaline earth metals in ammonia and the rates of the ensuing reactions with nickel(II) bromide are too rapid for accurate measurements, our experiments show qualitatively that both of these rates increase from lithium to cesium. Furthermore, the solubilities of the by-products (alkali bromides and amides) increase in the same direction. Thus, one obtains from the corresponding reactions, elemental nickel that is different in only one important respect, namely, surface area. This is shown by the fact that for the products obtained using lithium, sodium, potassium, rubidium and cesium as the reducing metals, catalytic activity per unit surface area is substantially constant. The relative solubility of the by-products obtained using calcium obviated a rigorous comparison including this metal.

(1) This work was supported, in part, by the Office of Naval Research, Contract N6onr 26610.

(2) W. M. Burgess and F. R. Holden, This Journal, **59**, 459 (1937).

(3) W. M. Burgess and F. R. Holden, *ibid*, **59**, 462 (1937).

(4) W. M. Burgess and J. W. Eastes, *ibid*, **63**, 2674 (1941).

(5) W. C. Johnson and A. W. Meyer, *Chem. Revs.*, **8**, 273 (1931); *cf.* W. L. Jolly, *ibid*, **50**, 351 (1952).

Burgess and Eastes[4] have attributed the pyrophoric character of the elemental nickel so-produced to the presence of adsorbed hydrogen. While all of the products prepared in our studies were pyrophoric in a degree that increased from lithium to cesium, the corresponding quantities of adsorbed hydrogen per unit weight of metal showed no consistent trend.

Experimental

Materials.—Hexammminenickel(II) bromide was prepared as described by Watt.[6] All other materials were commercial reagent grade chemicals.

Reduction Reactions.—The equipment and procedures employed were in all respects the same as those described previously[7] except that lithium was maintained in an atmosphere of nitrogen prior to addition to the solution and suspension of nickel(II) bromide, and that rubidium and cesium were added in fragile glass ampoules that were subsequently crushed.

When samples of hexammminenickel(II) bromide of the order of 2.5 g. in 15-20 ml. of liquid ammonia at −33.5° were treated with alkali metals (*ca.* 10% in excess of that required for complete removal of bromide ion), both the rates of solution of the alkali metals and the rates of the ensuing reactions with the bromide were quite evidently dependent upon the alkali metal employed. *Approximate* total times that elapsed between the addition of the alkali metal and the disappearance of the blue color characteristic of solutions of these metals in ammonia were as follows: Li, 5 min.; Na, 20 sec.; K, 10 sec.; Rb, < 10 sec.; Cs, << 10 sec. Following completion of the reactions, the ammonia-insoluble products were washed with liquid ammonia, with ethanol, and thereafter handled out of contact with the atmosphere and under strictly anhydrous conditions.

Properties of the Reduction Products.—By methods previously described,[7] the highly pyrophoric ammonia-insoluble products were analyzed for nickel, nitrogen, bromine and

Table I

Properties of Products from the Reduction of Nickel (II) Bromide with Alkali Metals in Liquid Ammonia

	Ammonia-insoluble product				
Alkali metal	Ni, %	H_2, cc./g.	Surface area, $m.^2/g.$	Reaction rate	Rate/unit area
Li	82.3	17.6	30[a]	1.6	0.05
Na	93.6	7.5	27	3.1	.11
K	92.0	18.7	54	3.8	.07
Rb	90.4	10.4	105	8.8	.08
Cs	83.9	2.1	127	9.1	.07

[a] This value was determined using a sample washed with liquid ammonia but not with ethanol and involves a correction for an initial rapid uptake of ammonia during the surface area determinations. This was attributed to the ammonation of impurities present and the validity of this procedure was confirmed by a surface area estimate obtained from electron photomicrographs of an ethanol-washed product which showed an average particle radius of 88 Å. and led to a computed surface area of 38 $m.^2/g.$

(6) G. W. Watt, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., 1950, p. 194.

(7) G. W. Watt, W. F. Roper and S. G. Parker, This Journal, **73**, 7591 (1951).

alkali metal after washing with ammonia, and usually only for nickel following washing with ethanol. In addition to surface area measurements, the quantities of hydrogen associated with the reduction products were determined. Catalytic activity was evaluated in terms of catalysis of the hydrogenation of allyl alcohol. The essential data are given in Table I, in which the catalytic activity of the nickel is expressed as the rate (in millimoles H_2 consumed/min./g. of catalyst) of the catalyzed hydrogenation reaction and the numerical values of which are taken from those portions of the corresponding rate curves over which the rates were substantially linear with time. In all cases this condition prevailed over at least three-fourths of the total reaction time.

Reduction Reactions Employing Calcium.—Similar reduction reactions employing excess calcium occurred at about the same rate as those involving lithium. Owing to the insolubility of calcium amide[8] and calcium bromide,[9] purification of the nickel by washing with liquid ammonia was ineffective. The composition of a typical ammonia-insoluble product was as follows: Ni, 17.4; Br, 44.0; N, 21.4; Ca, 11.7. Although 16% excess calcium was used in this particular case, unreacted hexammminenickel(II) bromide was present. Washing with ethanol was only partially effective as a means of purification and no means was found to purify the products without eliminating the catalytic activity of the elemental nickel present.

(8) F. W. Bergstrom, *Ann.*, **515**, 34 (1934).
(9) M. Linhard and M. Stephan, *Z. physik. Chem.*, **167**, 87 (1933).

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"The Catalytic Activity of Metals Produced by the Reduction of Salts in Liquid Ammonia. II. Ruthenium and Rhodium."

By George W. Watt, Archie Broodo, and W. A. Jenkins, Jr.

(Manuscript to be submitted for publication in The Journal of the American Chemical Society.)

Abstract

The reduction of ruthenium(III) iodide with potassium in liquid ammonia at -33.5° results in complete removal of iodine, the concomitant evolution of small quantities of hydrogen, and the formation of an ammonia-insoluble product which consists principally of elemental ruthenium. Although the composition of the insoluble solid product is not strictly reproducible, its activity as a catalyst for the hydrogenation of olefins is remarkably constant. Similarly, the reduction of bromopentamminerhodium(III) bromide with potassium yields elemental rhodium in relatively pure form which is an exceptionally effective catalyst for the hydrogenation of not only olefins but also aromatic nitro compounds. The reduction of the bromide is not complicated by side reactions involving potassium amide, since the action of this reagent upon the bromide in independent experiments has been shown to yield rhodium(III) amide.

August 31, 1953
GWW:dn

"The Catalytic Activity of Metals Produced by the Reduction of Salts in Liquid Ammonia. III. Palladium"

By George W. Watt, Archie Broodo, and S. G. Parker

(Manuscript to be submitted for publication in The Journal of the American Chemical Society.)

Abstract

The reduction of trans-dibromodiamminepalladium(II) with potassium in liquid ammonia at -33.5° occurs strictly in accordance with the equation:

$$Pd(NH_3)_2Br_2 + 2K \rightarrow Pd + 2KBr + 2NH_3$$

whereas the reaction of the same bromide with potassium amide in ammonia yields palladium(II) amide. The elemental palladium prepared as indicated above is stable when exposed to the atmosphere and/or water, and its catalytic activity (as applied to hydrogenation reactions) is of a high order and roughly comparable to rhodium prepared in a similar manner. The catalytic activity of palladium prepared in ammonia is far greater than that of the conventional "spongy palladium". The thermal decomposition of palladium(II) amide yields palladium, ammonia, and nitrogen, and there is no evidence for intermediation of either an imide or nitride of palladium.

August 31, 1953
GWW:dn

"Evidence for the Existence of an Ammine of Platinum(O)"

By George W. Watt, M. T. Walling, Jr., and Peggy I. Mayfield

(Manuscript accepted for publication in The Journal of the American Chemical Society.)

Abstract

The reduction of tetrammineplatinum(II) bromide with potassium in liquid ammonia at its boiling point is best interpreted as involving the addition of two electrons to the 4-coplanar tetrammineplatinum(II) ion to form a neutral tetrammine of platinum(O). Decomposition of this product yields only ammonia and platinum; the latter is an effective catalyst for the hydrogenation of olefins. The interaction of tetrammineplatinum(II) bromide and potassium amide in liquid ammonia yields platinum(II) amide 2-ammonate.

August 31, 1953
GWW:dn

"Pentammineiridium(O)"

By George W. Watt and Peggy I. Mayfield

(Manuscript accepted for publication in The Journal of the American Chemical Society.)

Abstract

The reduction of bromopentammineiridium(III) bromide with potassium in liquid ammonia at its boiling point results in complete removal of bromine and the formation of ammonia-insoluble pentammine-iridium(O). Thermal decomposition of this product produces only ammonia and iridium; the latter is effective as a catalyst for the hydrogenation of olefins. The reaction between bromopentammine-iridium(III) bromide and potassium amide in liquid ammonia yields iridium(III) amide 1-ammonate.

August 31, 1953
GWW:dn

"Kinetics of the Hydrogenation of Olefins over Adams Platinum Catalyst"

By George W. Watt and M. T. Walling, Jr.

(Manuscript to be submitted for publication in The Journal of Physical Chemistry.)

Abstract

The role of (a) weight of catalyst, (b) hydrogen pressure, (c) temperature, (d) agitation efficiency, (e) concentration of acceptor, and (f) concentration of product, as determinants in the rate of hydrogenation of olefins over Adams platinum catalyst has been determined. The reactions are first order with respect to hydrogen pressure, zero order with acceptor concentration in the case of hexene-1, but of no simple kinetic order in the case of allyl alcohol. The rates are independent of product concentration. Activation energies are within the range 500-2500 cal./mole. In both cases, rates increase linearly with the weight of catalyst where small weights are involved, but approach a limiting rate as the weight of catalyst is increased. Equations have been derived to relate reaction rate to the weight of catalyst/unit weight of acceptor and the resulting relationship has been applied with reasonably satisfactory results to data relating to catalysts other than Adams platinum.

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THE LOWER OXIDATION STATES OF ALUMINUM[1]

Sir:

Evidence for the existence of the +2 and +1 oxidation states of aluminum includes demonstration of the existence of certain compounds prepared in the absence of solvents,[2] spectroscopic evidence,[3] and data relating to the anodic oxidation of aluminum in liquid ammonia and other solvents.[4] Thermochemical considerations[5] also indicate that these oxidation states should exhibit appreciable stability even in the form of the crystalline halides.

We wish to make a preliminary report on what we believe to be conclusive evidence for the existence of these oxidation states in solution, based upon potentiometric titrations of liquid ammonia solutions of aluminum(III) iodide with liquid ammonia solutions of potassium using the equipment and procedures described previously.[6]

In a typical experiment, 8.31×10^{-4} g. eq. wt. of pure aluminum(III) iodide dissolved in *ca.* 45 ml. of anhydrous liquid ammonia was titrated with 8.56×10^{-2} *M* potassium solution. The titration curve shows two quite distinct end-points which correspond to the addition of 3.25 and 6.60 ml. of the potassium solution; the calculated volumes required for reduction of Al^{+3} to Al^{+2} and Al^{+1} are 3.24 and 6.49 ml., respectively.

Following the end-point corresponding to completion of reduction to Al^{+2}, a trace of white crystalline solid appears, the potential decreases gradually, then increases until the end-point corresponding to Al^{+1} is reached. A similar trend is observed following reduction to Al^{+1}. In view of the known chemistry of Al^{+3} in liquid ammonia,[7,8] it seems reasonable to attribute this behavior in both instances to the occurrence of slow ammonolytic reactions resulting in the separation of ammonobasic salts. Finally, when a slight excess of potassium over that required for reduction to Al^0 is added, the potential increases *ca.* 1200 mv. and this is coincident with the appearance of a permanent blue coloration which is too intense to be attributable to an ammonia solution of aluminum.[5]

These and related experiments will be described in more detail in a later communication. We are presently extending this method to the study of the intermediate oxidation state problem with other Group III elements, and those of both the lanthanide and actinide series.

(1) This work was supported, in part, by the Office of Naval Research Contract N6onr-26610.

(2) G. Grube, A. Schneider, U. Esch and M. Flad, *Z. anorg. Chem.*, **260**, 120 (1949).

(3) L. M. Foster, A. S. Russell and C. N. Cochran, THIS JOURNAL, **72**, 2580 (1950).

(4) For review and primary references see J. Kleinberg, "Unfamiliar Oxidation States and Their Stabilization," University of Kansas Press, Lawrence, Kan., 1950, p. 16; *cf.* Kleinberg, *et al.*, THIS JOURNAL, in press.

(5) F. Izmann, *Helv. Chim. Acta*, **33**, 1449 (1950).

(6) G. W. Watt and J. B. Otto, Jr., *J. Electrochem. Soc.*, **98**, 1 (1951).

(7) E. C. Franklin, THIS JOURNAL, **37**, 847 (1915).

(8) A. D. McElroy, J. Kleinberg and A. W. Davidson, *ibid.*, **72**, 5178 (1950).

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POTENTIOMETRIC TITRATION OF HALIDES OF ALUMINUM, GALLIUM, INDIUM AND THALLIUM WITH POTASSIUM IN LIQUID AMMONIA[1,2]

By George W. Watt, James L. Hall and Gregory R. Choppin

Department of Chemistry, The University of Texas, Austin, Texas

Received November 28, 1952

The potentiometric titration of the iodides of gallium(III) and indium(III) with solutions of potassium in liquid ammonia provides evidence only for the three-electron changes resulting in the formation of the corresponding elemental metals. Similar titrations involving thallium(III) chloride are complicated by the fact that the elemental thallium first produced competes in the reduction of the +3 chloride. These studies provide evidence for the formation of Tl_2^{+1}; elemental thallium is the end-product of the reduction reaction. Further studies on the potentiometric titration of aluminum(III) iodide with liquid ammonia solutions of potassium and potassium amide and different possible reaction mechanisms are considered. The reaction with potassium amide produces aluminum(III) amide which is thereafter converted to potassium ammonoaluminate.

This paper is concerned with results obtained in studies involving a novel approach to the detection and characterization of unusual oxidation states of the elements. The method in question consists of the potentiometric titration of liquid ammonia solutions of appropriate salts of higher oxidation states of the elements with standard solutions of alkali or alkaline earth metals in liquid ammonia. The titrations are conducted below the normal boiling point of ammonia (*e.g.*, −38 to −40°) in an anhydrous and oxygen-free system using equipment and procedures substantially identical with those described by Watt and Otto.[3]

Experimental

Materials.—With the exceptions noted below, all materials employed in this work consisted of reagent grade chemicals.

Aluminum(III) iodide was prepared by direct union of the elements by a method especially designed to yield a product free of elemental iodine. This procedure will be described elsewhere.[4]

Anal. Calcd. for AlI_3: Al, 6.6; I, 93.4. Found: Al, 6.5; I, 93.2.

Gallium(III) iodide was prepared by essentially the method described by Johnson and Parsons.[5]

Anal. Calcd. for GaI_3: I, 84.5. Found: I, 84.5.

With only minor modifications, the method of Johnson and Parsons was also used in the preparation of indium(III) iodide.

Anal. Calcd. for InI_3: I, 77.6. Found: I, 77.6.

In the absence of a satisfactory procedure for the preparation of either the iodide or bromide of thallium(III), the corresponding chloride was obtained from the City Chemical Corporation and used without further purification despite its lesser solubility in liquid ammonia.

Methods.—Since the equipment and procedures involved in carrying out the potentiometric titrations have been described in considerable detail elsewhere[3] they need not be discussed here except to point out that the initial volume of the liquid ammonia solutions titrated was in all cases approximately 50 ml. Reactions carried out on a larger scale and having as their objective the isolation and identification of intermediates and/or final products employed equipment and techniques of the type described by Watt and Keenan.[6]

Titration of Thallium(III) Chloride.—A solution and suspension of 0.91 meq. of thallium(III) chloride and 2.61 meq. of sodium chloride (in solution, as a supporting electrolyte) was titrated with a 0.0586 *M* solution of potassium in liquid ammonia. The data for a typical case are given in Fig. 1. When the first portion of potassium solution was added a

(1) This work was supported in part by the Office of Naval Research, Contract N6onr-26610.

(2) Presented at the Symposium on Liquid Ammonia Chemistry, September, 1952, Meeting of the American Chemical Society, Atlantic City, N. J.

(3) G. W. Watt and J. B. Otto Jr., *J. Electrochem. Soc.*, **98**, 1 (1951).

(4) G. W. Watt and J. L. Hall, "Inorganic Syntheses," Vol. IV, in press.

(5) W. C. Johnson and J. B. Parsons, This Journal, **34**, 1210 (1930).

(6) G. W. Watt and C. W. Keenan, *J. Am. Chem. Soc.*, **71**, 3833 (1949).

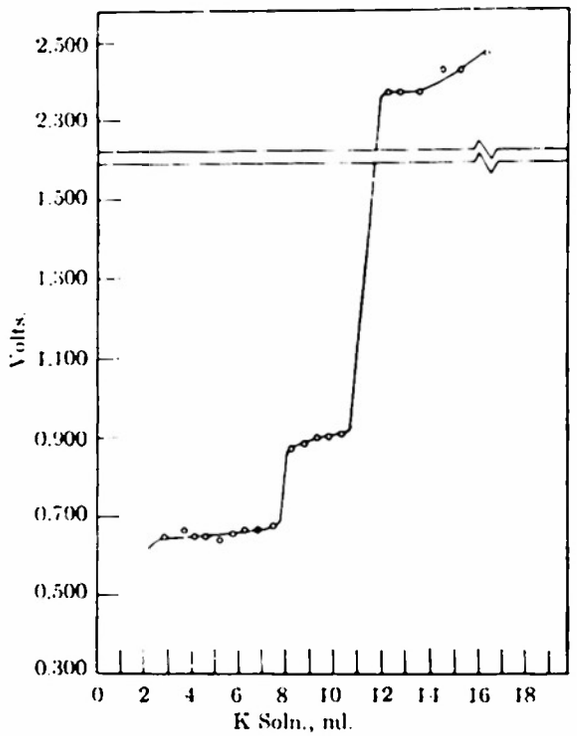

Fig. 1.—Potentiometric titration: thallium(III) chloride with potassium.

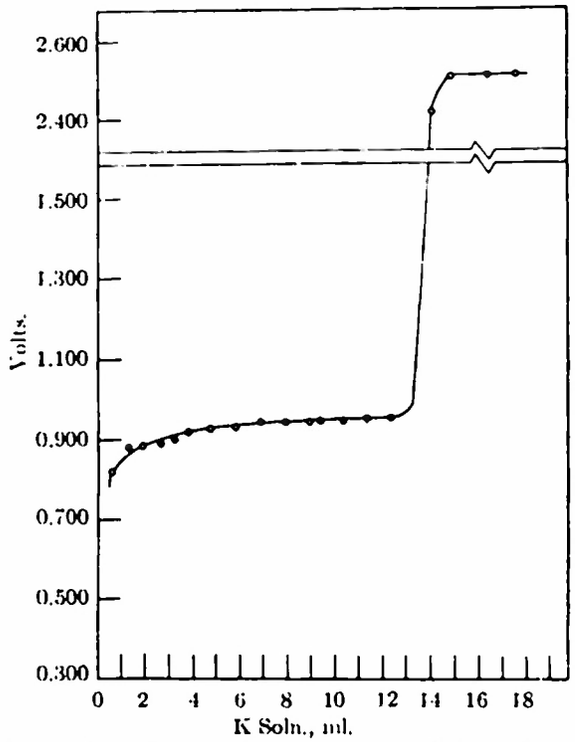

Fig. 2.—Potentiometric titration: indium(III) iodide with potassium.

black precipitate formed but rather quickly disappeared. As the titration proceeded, however, the rate of disappearance of this product decreased; some of it agglomerated and settled to the bottom of the reactor where it thereafter reacted slowly if at all. Finally, upon addition of potassium solution in excess of that required for complete reduction to elemental thallium, the solution assumed the characteristic blue color of solutions of alkali metals in ammonia and the accompanying increase in potential was that characteristic of such solutions.[3] The blue color, however, was not permanent, but it decreased in intensity only slowly. The ammonia-insoluble product of the reduction reactions was identified as elemental thallium by means of an X-ray diffraction pattern obtained using CuKα radiation, a nickel filter, a tube voltage of 30 kv., a filament current of 15 ma. and an exposure time of 4 hr. Found (relative intensities in parentheses): d = 2.62 (strong), 1.72 (medium) and 1.57 (medium). The corresponding values from the literature[7] are: d = 2.62 (1.00), 1.73 (0.3) and 1.57 (0.5).

Titration of Indium(III) Iodide.—A solution containing 0.70 meq. of indium(III) iodide was titrated with a liquid ammonia solution 0.0498 *M* with respect to potassium (see Fig. 2). Upon the first addition of potassium solution there appeared a black precipitate of elemental indium which continued to form as the titration proceeded.

Titration of Gallium(III) Iodide. The titration of a solution of 0.49 meq. of gallium(III) iodide with 0.0403 *M* potassium solution to form elemental gallium (Fig. 3) proceeded in a manner substantially identical with that described for indium.

Titration of Aluminum(III) Iodide.[8]—In a typical case, 0.83 meq. of aluminum(III) iodide in solution in liquid ammonia was titrated with 0.0541 *M* potassium solution (see Fig. 4). As the progress of the titration approached the first minimum shown in the curve (Fig. 4) a very finely divided gray-white solid began to separate from the solution and this persisted throughout the remainder of the titration. After the addition of that increment of potassium solution which provided the first excess of alkali metal, the blue potassium solution and the gray-white solid coexisted apparently without change over periods greater than five hours.

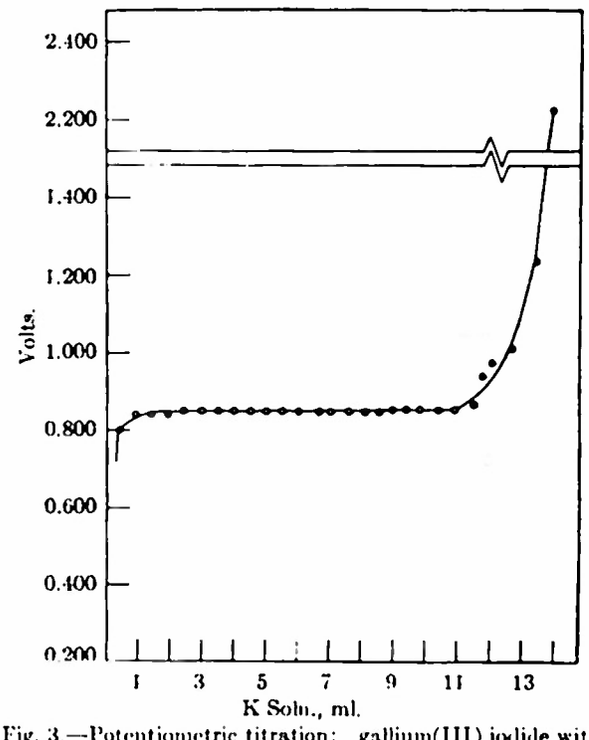

Fig. 3.—Potentiometric titration: gallium(III) iodide with potassium.

In order to choose between different possible mechanisms that might be compatible with experimental results of the type shown in Fig. 4, it would be helpful to know whether any hydrogen is evolved during the course of the reduction reactions. It is impractical to attempt to secure this information from the potentiometric titration runs since the solutions that are titrated are stirred by means of a stream of anhydrous oxygen-free nitrogen that is presaturated with

(7) A.S.T.M. Index of X-Ray Diffraction Patterns.

(8) *Cf.* G. W. Watt, J. L. Hall and G. R. Choppin, *J. Am. Chem. Soc.*, **73**, 5920 (1951).

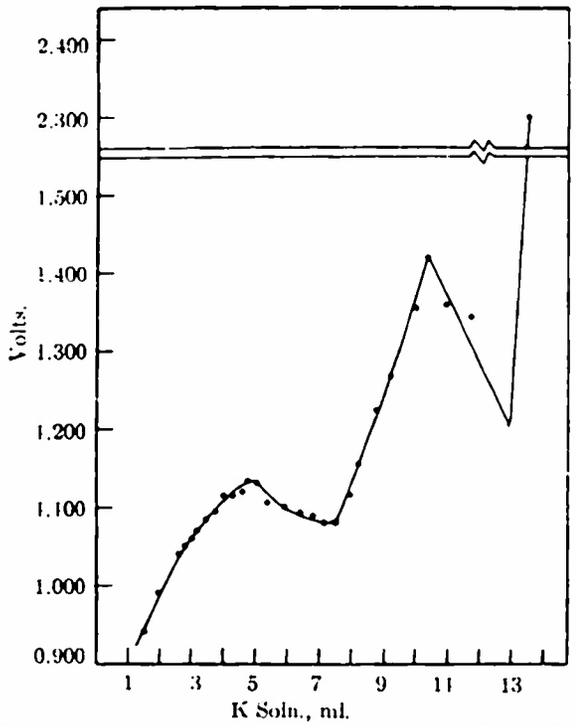

Fig. 4.—Potentiometric titration: aluminum(III) iodide with potassium.

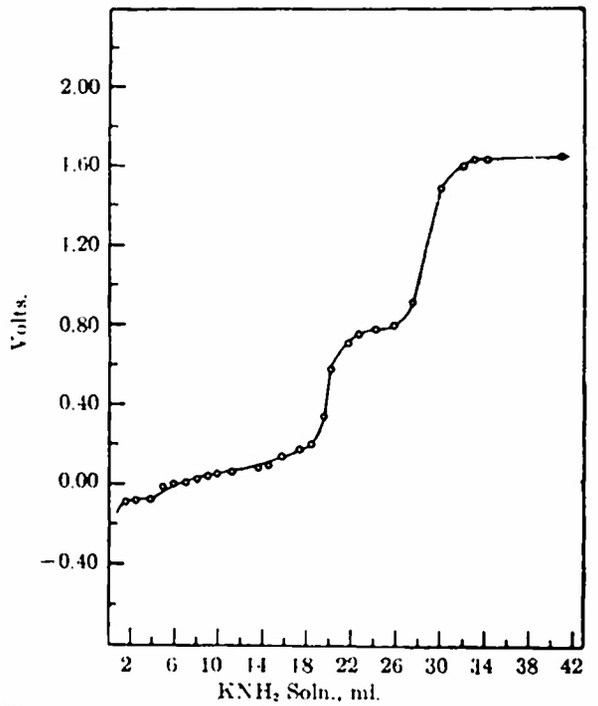

Fig. 5.—Potentiometric titration: aluminum(III) iodide with potassium amide.

ammonia.[3] Hence if hydrogen were formed, its volume would be negligible in relation to the volume of nitrogen collected and the measurement of the quantity of hydrogen would be quite inaccurate. Accordingly, this difficulty was overcome by reducing aluminum(III) iodide with potassium solution on a considerably larger scale using equipment of the type described previously[4] which provides for stirring with a stream of ammonia only and for the collection and analysis of water-insoluble gases. In four separate experiments, 4.5, 4.0, 7.2 and 2.5 meq. of aluminum(III) iodide (each sample in an initial volume of approximately 40 ml. of liquid ammonia) were titrated with, respectively, 0.19, 0.22, 0.64 and 0.34 *M* potassium solutions. The major variable in these four experiments was the rate of addition of the potassium solutions which was varied (respectively) from *ca.* 7 to 0.5 hr. Although the four results were not entirely internally consistent, the volumes of hydrogen collected during the course of the reduction reactions varied from 0 to > 100% of that calculated on the assumption that all of the potassium added reacted to form an equivalent quantity of hydrogen. Further, the volume of hydrogen formed appears to depend upon the rate at which the potassium solution is added.

Titration of Aluminum(III) Iodide with Potassium Amide.—In other experiments potentially of importance in the interpretation of the reduction reactions described above, 1.06 meq. of aluminum(III) iodide in *ca.* 50 ml. of liquid ammonia solution was titrated with 0.0478 *M* potassium amide solution. The resulting data are shown in Fig. 5

Discussion

In view of the well established stability of the Tl^{+1} it was anticipated that the potentiometric titration of thallium(III) chloride with potassium might at least give evidence of the successive formation of Tl^{+1} and Tl^0. For the case shown in Fig. 1, corresponding changes in potential should occur upon addition of 10.3 and 15.5 ml. of potassium solution. However, the reaction that occurs as the result of the addition of the first 2.2 ml. of potassium solution (see Fig. 1) evidently involves the partial reduction of Tl^{+3} to black ammonia-insoluble Tl^0 which in turn reacts fairly rapidly to reduce some of the remaining Tl^{+3} to Tl^{+1} and/or Tl^{+2}. The reaction between Tl^0 and Tl^{+3} seems more probable than a possible interaction of Tl^0 and the solvent[9] since the rate at which the Tl^0 reacts appears to decrease progressively as the supply of Tl^{+3} decreases. Following the addition of 2.2 ml. of potassium solution, the black solid (identified as elemental thallium at the end of the run) was present as a solid phase in increasing quantity as the titration progressed and it appeared to react only relatively slowly for a time and finally not at all. Owing to the interference by this concurrent reaction involving Tl^0, it is not to be expected that the two subsequent changes in potential could be correlated strictly with the anticipated stoichiometry corresponding to possible intermediates in the reduction process. Thus in the case of the data of Fig. 1, it is apparently fortuitous that the increase in potential amounting to 0.2 v. that occurs upon addition of 8.0 ml. of potassium solutions agrees well with the value of 7.8 ml. calculated on the assumption that the Tl^0 first produced then reduces Tl^{+3} to Tl^{+2} and Tl^{+1}. Actually, this increase in potential probably corresponds to the completion of reduction to Tl^{+1} but is displaced to the left owing to reduction attributable to Tl^0. In effect, the intermediation of reduction reactions involving the freshly precipitated Tl^0 renders the data for the remainder of the titration almost impossible of rigorous interpretation. Furthermore, it has been found that data of the type shown in Fig. 1 are not strictly reproducible; the same changes in potential are observed from run to run but the relative positions

(9) A. D. McElroy, J. Kleinberg and A. W. Davidson, *J. Am. Chem. Soc.*, **74**, 738 (1952); *cf.* C. A. Seely, *via* Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. V, Longmans, Green and Co., New York, N. Y., 1937, p. 421.

at which these changes occur are somewhat subject to variation.

The data shown in Figs. 2 and 3 indicate that the reduction of the iodides of indium(III) and gallium(III) involves only the three-electron changes corresponding to reduction to the respective elemental metals. Evidently the +2 and +1 oxidation states of these elements are not stable in liquid ammonia under the conditions involved in these experiments. These results are somewhat surprising in view of existing evidence for these lower oxidation states in liquid ammonia, other solvent media and in the solid state.[10]

The results obtained in the potentiometric titration of aluminum(III) iodide with potassium have previously been interpreted[5] as evidence for the existence of the +2 and +1 oxidation states of aluminum. With reference to Fig. 4, for example, the calculated volumes of potassium solution required for reduction of Al^{+3} to Al^{+2} and Al^{+1} are 5.1 and 10.2 ml., respectively. An inspection of Fig. 4 shows that the experimental results are in excellent agreement with these values and the reproducibility of these results has been amply demonstrated.

It has been suggested, however, that these results might also be explained in terms of a series of acid-base equilibria,[11] *e.g.*

$$Al^{+3} + NH_3 \rightleftharpoons AlNH_2^{+2} + NH_4^+$$

$$AlNH_2^{+2} + NH_3 \rightleftharpoons Al(NH_2)_2^{+1} + NH_4^+$$

$$Al(NH_2)_2^{+1} + NH_3 \rightleftharpoons Al(NH_2)_3 + NH_4^+$$

wherein the observed changes in potential could correspond successively to the three aluminum-containing species shown above. Thus it is proposed in effect that the aluminum(III) iodide is ammonolyzed and that the reaction that occurs upon addition of potassium is that with NH_4^+ to liberate hydrogen. Our experiments designed to determine whether hydrogen is evolved have led to results that are not satisfactorily conclusive. It appears that hydrogen is indeed evolved in substantially the stoichiometric quantity if the reaction is carried out rapidly but that the quantity of hydrogen liberated decreases as the time of addition of potassium solution is increased to as much as 7 hr. Since the potentiometric titration must be carried out very slowly (*e.g.*, periods of time of the order of 48 hr.) in order to ensure the re-establishment of equilibrium after each addition of potassium, there remains the question as to whether any hydrogen is produced in runs of the type that led to the data of Fig. 4. Additional experiments concerned with the questions of hydrogen formation and the identity of other ammonia-insoluble intermediate and final reduction products are in progress.

Two additional lines of evidence bearing upon the mechanism of the reduction of aluminum(III) iodide with potassium also merit consideration. If the data of Fig. 4 are to be interpreted in terms of ammonolysis, it might be expected that the same intermediate and final species should be formed by the reaction between aluminum(III) iodide and potassium amide in liquid ammonia. That such is clearly not the case is shown by the data of Fig. 5. The changes in potential that occur upon addition of 22.1 and 29.5 ml. of potassium solution conform almost exactly to the reactions

$$Al^{+3} + 3KNH_2 \longrightarrow Al(NH_2)_3 + 3K^+$$

$$Al(NH_2)_3 + KNH_2 \longrightarrow KAl(NH_2)_4$$

The white ammonia-insoluble aluminum(III) amide that is formed first then reacts with additional potassium amide to form a soluble salt of an amphoteric base. Finally, it should be pointed out that if aluminum(III) amide were the final product of the reduction of aluminum(III) iodide with potassium, any excess of the metal added would undoubtedly react with the insoluble amide to form one or more salts of this amphoteric base. It was observed, however, that solutions of potassium do not react with the end-product of the reduction reaction over periods up to several hours.

(10) For review and primary references see: J. Kleinberg, "Unfamiliar Oxidation States and Their Stabilization," University of Kansas Press, Lawrence, Kan., 1950; *J. Chem. Education*, **29**, 324 (1952).

(11) H. A. Laitinen, private communication.

August 31, 1953
GWW:dr

"Aluminum(I) Iodide"

By George W. Watt and James L. Hall

(Manuscript to be submitted for publication in The Journal of the American Chemical Society.)

Abstract

The reduction of one mole of aluminum(III) iodide with two gram-atoms of potassium in liquid ammonia at -33.5° yields a white ammonia-insoluble solid which contains only aluminum, iodine, and ammonia. Aluminum and iodine are present in exactly a 1:1 ratio; the ammonia is loosely bound and is lost slowly at room temperature. When heated to 800°, ammonia is the only gaseous product; the residual solid contains one gram-atom of potassium/gram-atom of iodine. The data indicate that the primary reduction product consists of the 3-ammonate of aluminum(I) iodide and the only contradictory evidence is the fact that this product fails to exhibit reducing properties.

August 31, 1953
GWW:dn

"Potentiometric Titration of Simple Salts with Potassium in Liquid Ammonia."

By George W. Watt, Gregory R. Choppin, and James L. Hall.

(Manuscript accepted for publication in The Journal of the Electrochemical Society.)

Abstract

By means of potentiometric titrations of solutions of salts with solutions of potassium in liquid ammonia at -38°, it has been shown that bismuth(III) iodide is reduced to Bi^{o}, K_3Bi_3, and K_3Bi_5 without intermediation of either the +2 or +1 oxidation state of bismuth. The reduction of Iron(II) bromide is very complex and apparently does not involve the intermediate formation of Fe^{+1}. The reduction of potassium nitrate involves only the reduction of nitrate ion to nitrite ion, followed by precipitation of potassium hydronitrite. Data relative to the reduction of cobalt(II) nitrate have permitted a choice between two possible reduction mechanisms previously proposed. The data presented in this paper clearly demonstrate the usefulness of the potentiometric titration technique in the study of the mechanism of inorganic reduction reactions in ammonia.

August 31, 1953
GWW:dn

"Potentiometric Titration of Ammines of Rhodium, Iridium, and Platinum with Solutions of Potassium and Potassium Amide in Liquid Ammonia"

By George W. Watt, Gregory R. Choppin, and James L. Hall

(Manuscript accepted for publication in The Journal of the Electrochemical Society.)

Abstract

Potentiometric titration of tetrammineplatinum(II) bromide with potassium in liquid ammonia at -38° shows that the reduction of this salt to tetrammineplatinum(O) is exactly a two electron change and that the +1 oxidation state of platinum is not an intermediate. Similar reduction of bromopentammineiridium(III) bromide is apparently more complex and leads to observed changes in potential that do not correspond to any reasonable or probable reactions. The titration of this same iridium salt with potassium amide solution, however, provides evidence for the stepwise replacement of bromide by amido groups followed by the conversion of the resultant iridium(III) amide to (probably) a potassium amidoiridate(III). Bromopentamminerhodium(III) bromide and potassium amide react similarly, but only to and including the formation of rhodium(III) amide.

August 31, 1953
GWW:dn

"Mechanism of the Reduction of Potassium Tetracyanonickelate(II) and Potassium Hexacyanocobaltate(III) with Potassium in Liquid Ammonia"

By George W. Watt, James L. Hall, Gregory R. Choppin and Philip S. Gentile.

(Manuscript accepted for publication in The Journal of the American Chemical Society.)

Abstract

Uncertainties remaining from earlier work on the reduction of potassium tetracyanonickelate(II) with potassium in liquid ammonia at -33.5° have been clarified by means of potentiometric titrations. Two one-electron steps are involved when the salt is in excess, and one two-electron reaction when potassium is in excess. Potassium tetracyanocobaltate(I) has been shown to be an intermediate in the reduction of potassium hexacyanocobaltate(III) to potassium tetracyanocobaltate(O).

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